

THE BASIC FACTORS OF  
ANODIC POLAROGRAPHY

By  
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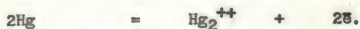
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## I. INTRODUCTION

Although the dropping mercury electrode is almost exclusively used as a cathode, it may be anodically polarized.\* In an indifferent aqueous electrolyte--a solution which neither forms complexes nor insoluble salts with mercurous and mercuric ions--a negative oxidation current\*\* appears at about +0.4 v. vs. the saturated calomel electrode (S.C.E.). In the region of +0.45 v. this current becomes comparatively large and increases exponentially. Ravenda<sup>9</sup> has suggested that this is due to the free dissolution of mercury from the dropping electrode:



Kolthoff and Miller<sup>6</sup> determined the polarographic slope for this process and found a value of 0.032 v. which is in reasonable agreement with the theoretical value of 0.0296 v. for a two electron change at the dropping mercury electrode (D.M.E.).

However, if the dropping mercury electrode is polarized anodically in the presence of an ion which either

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\*Anodic polarization refers to the application of a positive external potential to the D.M.E.

\*\*The term negative current indicates only the direction of the current. Normally in polarography a reduction occurs at the dropping mercury electrode and the direction of the current is said to be positive. When an oxidation is found at the dropping mercury electrode, the current is in the opposite direction and said to be negative.

complexes or forms insoluble mercury salts, the potential at which this negative current appears becomes less positive. The presence of this ion permits the oxidation of mercury at a lower potential. This shift in potential depends upon the stability of the insoluble or complexed mercury salt. The potential at which the dissolution of the mercury electrode begins is about  $-0.6$  v. in  $1$  M cyanide,  $-0.2$  v. for  $1$  M hydroxide and  $+0.1$  v. for  $1$  M chloride.<sup>7</sup> These ions are said to depolarize the dropping mercury electrode since their effect is to tend to prevent the polarization of the electrode.

Many of these depolarizing ions may be determined polarographically in a supporting electrolyte such as potassium nitrate. The amount of mercury oxidized at potentials less positive than  $+0.4$  v. at the dropping mercury electrode is dependent upon the diffusion of the depolarizer to the electrode and hence upon the concentration of the depolarizer. A limiting current is reached and maintained until a potential of  $+0.4$  v. is attained. For example, the electrode reaction at the dropping mercury anode in the presence of chloride ion<sup>5</sup> is



Work with anodic waves frequently is plagued with anomalies and unexplained phenomena. Kolthoff and Miller<sup>6</sup>



noted that in the presence of iodide concentrations greater than  $10^{-3}$  M the growth of the mercury drop is irregular, the diffusion current is poorly defined and the current fluctuates abnormally. Ravenda<sup>9</sup> observed a double wave in solutions containing bromide ion concentrations greater than  $10^{-3}$  M. In this case, the first limiting current remained at practically constant height with increasing concentration of bromide. Other experimenters have found similar difficulties with anions such as chloride<sup>5</sup>, thio-sulfate<sup>9</sup>, etc.

Other unexplained phenomena have recently been observed by Gropp<sup>4</sup> while electrolyzing solutions containing both chloride and bromide ions. In these solutions the number of waves observed and their positions varied with the concentrations of the halide ions.

Although frequently these anodic waves are of analytical importance their use is usually limited to a very small concentration range or they are completely valueless. Occasionally, the addition of a maximum suppressor is beneficial. However, the action of any maximum suppressor is but vaguely understood.

When the dropping mercury electrode is polarized as high as +1 v. with respect to the S.C.E., Bockris and Parsons<sup>2</sup> found that a black film forms upon the surface of the mercury in hydrochloric acid solutions. At times, the drops would fall only 1-2 cm trailing behind them a thin

black tube. Succeeding drops exuded regularly from this tube. Similar effects were observed in solutions of potassium chloride, potassium bromide, potassium iodide and sodium carbonate. These authors called this peculiar behavior at the electrode "the mercury tube effect."

A potential of +0.4 v. vs. S.C.E. has been accepted for many years as the limit of polarographically useful polarization of the dropping mercury electrode. This has been due to the observation of the exponentially increasing negative current, the agreement of the polarographic slope of this wave with the value predicted by theory for the oxidation of mercury to mercurous ion, and the peculiar electrode processes found at high positive potentials in the presence of some electrolytes. No polarographic work with a dropping mercury anode has been reported at potentials more positive than +0.4 v. with reference to the saturated calomel electrode.

Several years ago, Gropp<sup>4</sup> was able to exceed the +0.4 v. limit by at least 1.0 volt without the appearance of a large oxidation current. The experiment was performed in a potassium nitrate solution well purged of oxygen. This was accomplished by scrubbing the electrolyte with pure nitrogen for two or three hours.

More recently the author found that, in potassium nitrate solution at low galvanometer sensitivity (0.600 microamperes/mm), the so-called mercury dissolution wave leveled off. This was followed at still higher potentials by another wave which also reached a limiting current. Finally, at an anodic polarization between 1.6 and 2.1 v. the current rapidly increased exceeding the limit of the recording galvanometer.

The following studies resulted directly as an attempt to explain these observations and anomalies.

## II. APPARATUS AND TECHNIQUE

Apparatus. A Sargent-Heyrovsky Pen Recording Polarograph, Model XXI, was used in these studies. The details of operation, maintenance and specifications of the instrument may be found in the manual of instructions prepared by the manufacturer.<sup>1</sup> The drive motor of this instrument was operated on a 115 v. alternating current line stabilized by a constant voltage transformer to minimize line fluctuations.

The dropping mercury electrode used in conjunction with the polarograph was cut from a piece of marine barometer tubing which was obtained from The Corning Glass Works. The capillary was of such length as to give a drop-time of 3.0 to 3.5 seconds in a 0.1 M potassium nitrate solution with no potential applied and at a mercury head of 59 cm. The electrode assembly consisted of this capillary inserted into a rubber stopper and connected to a mercury reservoir with clean heavy-walled neoprene tubing.

Four types of electrolysis vessels were used: (1) a Heyrovsky cell, (2) an H-cell with an agar bridge, (3) a modified H-cell with no agar bridge, and (4) a cell similar to (3) but with a conically shaped pool electrode section. Figures 1 and 2 show, respectively, these latter two cells. Henceforth, reference to the above cells will be by number.



Figure 1. Cell (3) is an H-cell which has no agar bridge.

A potassium nitrate supporting electrolyte was used in much of this work. To reduce the number of species of ions to a minimum, cell (2) had the reference electrode prepared from mercury in contact with 0.1 M potassium nitrate. This half-cell has been found to maintain a constant potential over a period of several months of +0.079 v. as measured against a S.C.E. with a potentiometer. The agar bridge of this cell had 0.1 M potassium nitrate as the electrolyte in 5% agar.

Cell (3) is shown in Figure 1. This cell is essentially a Heyrovsky cell except that the mercury falling from the dropping electrode is maintained apart from the mercury pool electrode. This minimizes contamination of the mercury by electrode reaction products formed at the dropping mercury electrode. The cell has about the same dimensions as a conventional H-cell and hence will have approximately the same electrical resistance. The resistance of the entire electrode assembly with a 0.1 M potassium nitrate solution in the cell was measured on an a.c. bridge and found to be 4200 ohms.

Figure 2 is a diagram of cell (4). This cell has been further modified to permit variation of the area of the mercury pool electrode surface. This was accomplished by drawing out one side of an H-cell into a cone. The diameter was determined at various places along the cone



Figure 2. Cell (4) is an H-cell in which the area of the pool electrode may be varied.



by allowing drill bits to come to rest in the cone and marking these positions. By filling the cone to different levels with mercury the area of the electrode may be changed and computed. These areas were calculated from the diameter of the cell assuming that the conical section is a perfect circle and disregarding the additional surface area from the formation of the mercury meniscus.

Chemicals. With the exception of the mercury and the thallous nitrate all chemicals used in these studies were reagent grade. The mercury was repurified according to the procedure given by Dayan.<sup>3</sup> The thallous nitrate was Fisher Scientific Company's "purified" grade.

Procedure. The general procedure for obtaining the polarograms is discussed in the following paragraphs. In some cases it was desirable to obtain polarograms of solutions containing oxygen. In these instances the deoxygenation portion of the method was omitted.

A pool of pure mercury is poured to a depth of about a centimeter into one side of a clean, dry cell (3). With the stopcock open, 0.1 M potassium nitrate solution is allowed to half-fill both compartments of the cell. The dropping mercury electrode is fitted into place and the pool compartment is closed with a rubber stopper. A newly cleaned cell and a fresh mercury pool is used for each experiment.



In some cases it is necessary to expel the oxygen from the cell and the solution. This is achieved by bubbling nitrogen through the solution prior to the electrolysis and over the solution during the polarographing. The nitrogen from the tank is first passed over hot copper ( $350^{\circ} - 400^{\circ}\text{C}$ ) to remove residual oxygen and then bubbled through a small tower containing the same electrolyte as is in the cell to presaturate the gas. The presaturation prevents changes in the concentration of the electrolyte in the cell. A bubble time of 20 to 30 minutes at a rate of about two bubbles per second is required to reduce the oxygen concentration to a usable level.

A three-way stopcock is placed in the nitrogen line. One piece of tubing leads the nitrogen to a gas inlet tube near the top of the dropping mercury electrode section of the cell. This is used to keep a flow of nitrogen over the solution during a run. The second outlet of the stopcock permits gas to be bubbled through the pool compartment and is employed to remove oxygen from the solution and the cell.

It is desirable to remove oxygen from both sides of the cell at the same time. To do this a rubber tube is attached to the gas outlet near the top of the pool section and to the lead-in tube admitting gas to the bottom of the dropping electrode compartment. The stopcock between the

two halves of the cell is closed to prevent pushing the solution from one compartment to the other. Since a little of the solution is trapped in the stopcock, this is opened for a few seconds about every five minutes of the bubble period. The nitrogen escapes from a small slit cut in the stopper holding the dropping mercury electrode.

Upon completion of the bubbling, nitrogen is diverted over the electrolyte surface instead of through the solution. The stopcock is opened and the nitrogen entry tube is replaced with the negative potential lead from the polarograph. The positive lead is attached to the mercury reservoir. The mercury reservoir is then adjusted to a height of 59 centimeters. The polarogram is now recorded.

The room is air conditioned and the temperature is maintained between 25° and 27°C. The polarograph is fitted with damping condensers. Maximum damping is always used. All polarograms are recorded with the dropping mercury electrode as the anode at a sensitivity of 0.600 microamperes per millimeter unless specifically stated otherwise.

Capillary Constants. The electrode capillary constant,  $m^{2/3}t^{1/6}$ , was determined at several applied potentials. One hundred drops of mercury were collected at each potential in a special polarographic cell fitted with a small funnel to keep the collected drops apart from the mercury pool electrode. This cell is shown in Figure 3. The supporting

electrolyte was oxygen free 0.1 M potassium nitrate. Data and the calculated constant,  $m^{3/4}t^{1/6}$ , are found in Table I. All values are averages of at least two determinations.

TABLE I  
VARIATION OF THE CAPILLARY CONSTANT,  $m^{3/4}t^{1/6}$ , WITH APPLIED POTENTIAL

Applied Potential Volts	Polarity of D.M.E.	Mass of Hg (m) mg	time (t) sec	$m^{3/4}t^{1/6}$
1.0	negative	3.027	2.730	2.474
0.0	- -	3.045	2.914	2.510
0.5	positive	3.039	2.221	2.396
1.0	positive	3.026	2.035	2.355

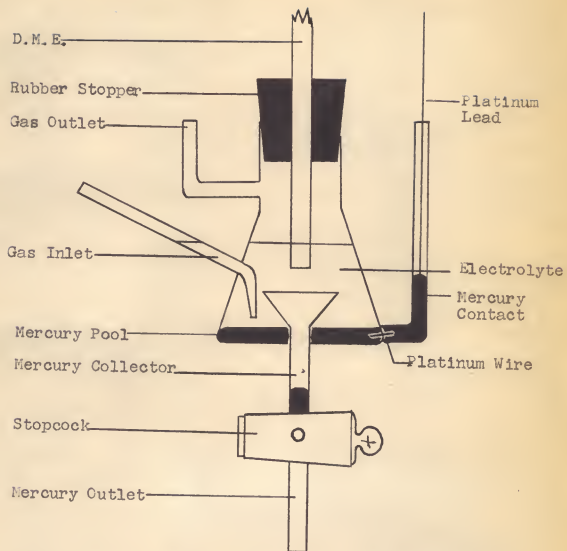


Figure 3. Cell used for determining the capillary constant.

### III. RESULTS AND DISCUSSION

Relationship between the Mercury Dissolution Wave and Oxygen. Three related experiments were performed with the dropping mercury electrode anodically polarized in a 0.1 M potassium nitrate supporting electrolyte. The first set of experiments were run in a Heyrovsky cell, the second, in the H-cell with the mercury-0.1 M potassium nitrate reference half-cell, and the third, in the modified H-cell with a liquid bridge of supporting electrolyte. Each of these experiments has demonstrated independently that +0.4 v. with respect to a S.C.E. is not a limiting value of polarization of the dropping mercury electrode. This potential was exceeded by at least another 1.5 v. before the current increased exponentially. The apparent limit was related to the presence of oxygen in the cell and required high recorder shunt ratios to be observed as long as this oxygen was present.

Figure 4 shows the electrolysis of a solution 0.1 M in potassium nitrate and oxygen in equilibrium with the atmosphere in a Heyrovsky cell. At this low recorder sensitivity the so-called mercury dissolution wave did not continue to increase exponentially as has always been stated previously in the literature. Instead, a large polarographic wave and maximum were formed. As the potential was further increased a second wave followed

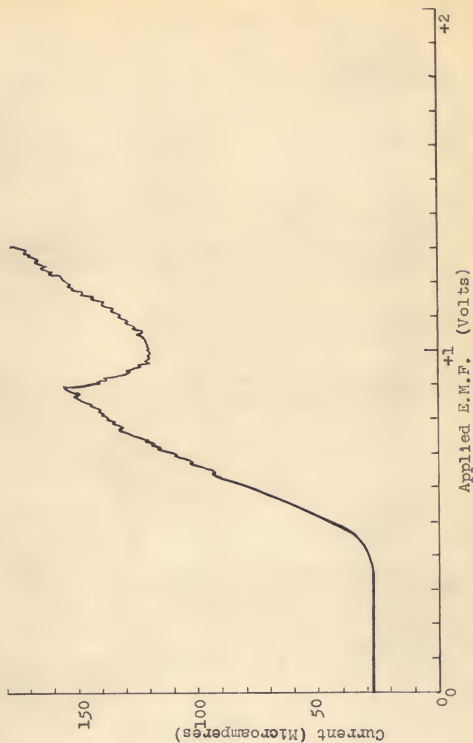


Figure 4. Polarogram of 0.1 M  $\text{KNO}_3$  solution with oxygen in equilibrium with the air in a Heyrovsky cell.

and finally, at about 1.6 v. applied the current became so large that it could no longer be recorded. The entire polarogram appeared quite erratic and ill-defined. This was due, at least in part, to the irregular mercury drop formation.

Upon removal of the oxygen from the solution by sweeping the cell and its contents for twenty minutes with pure nitrogen gas, the current drawn during electrolysis over the same potential span was very much decreased as shown in Figure 5. In fact, a very definite diffusion flat was obtained. Furthermore, the formation of the mercury drops now occurred periodically.

Some of the difficulties observed seemed to be due to inconsistent electrode processes at the mercury pool. These were overcome by using the H-cell previously described and identified as cell (2). This cell permitted separation of the pool electrode from the mercury which fell from the dropping electrode.

Electrolysis in cell (2) of 0.1 M potassium nitrate solution in equilibrium with oxygen of the air showed two well defined waves. The first was at approximately +0.56 v. applied and the second at +1.46 v. These waves are shown in Figure 6. A maximum appeared on the first wave and the second wave was drawn out (has a large polarographic slope) over a wide span of applied E.M.F. At about +2.3 v.

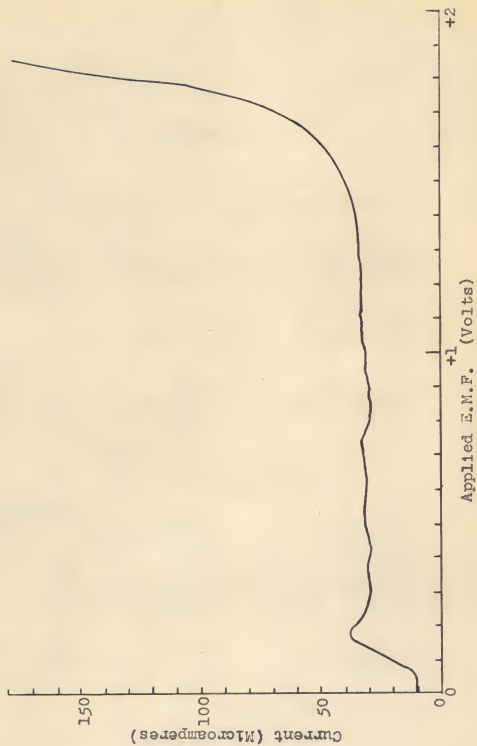


Figure 5. Polarogram of 0.1 M  $\text{KNO}_3$  (oxygen free) in a Heyrovsky cell.



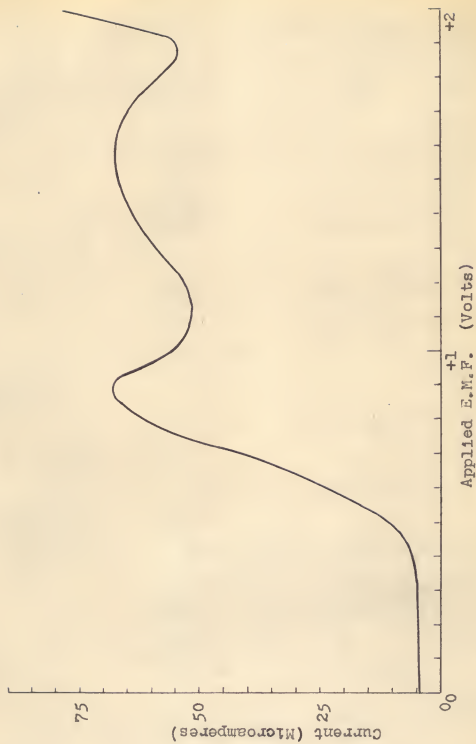


Figure 6. Polarogram of 0.1 M potassium nitrate in an H-cell  
{cell (3)}

applied, the current drawn increased rapidly exceeding the current limit of the recorder.

When the same solution was run and then re-run several times in succession, the two waves decreased markedly in height. The decrease was rapid at first, but seemed to approach a limit after completion of three or four polarizing cycles. Subsequent cycles effected only very small further changes. These polarograms are illustrated in Figure 7. However, when the solution was allowed to stand idle for a period of an hour or so and then electrolyzed again, the waves increased in height.

Removal of oxygen from the dropping mercury electrode compartment of the cell had little, if any, effect upon the two anodic waves. However, when oxygen was removed from the reference half-cell, no waves were found before +1.8 v. applied. Beyond +1.8 v. the current increased rapidly and went off scale. This occurred independently of the presence of oxygen in the dropping mercury electrode side of the cell. This is demonstrated in Figure 8.

In the third type of cell, previously listed as cell (3), the results were entirely similar. This type of cell had the two sections of the 'H' connected by the supporting electrolyte. In the presence of oxygen the two waves appeared as before, decreased in height upon subsequent runs and disappeared entirely in the absence of oxygen.

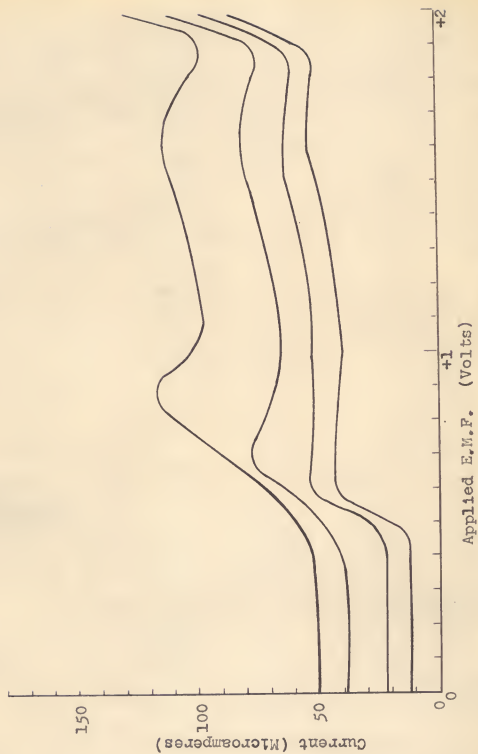


Figure 7. Successive Polarograms of 0.1 M  $\text{KNO}_3$  electrolyzed in cell (2).

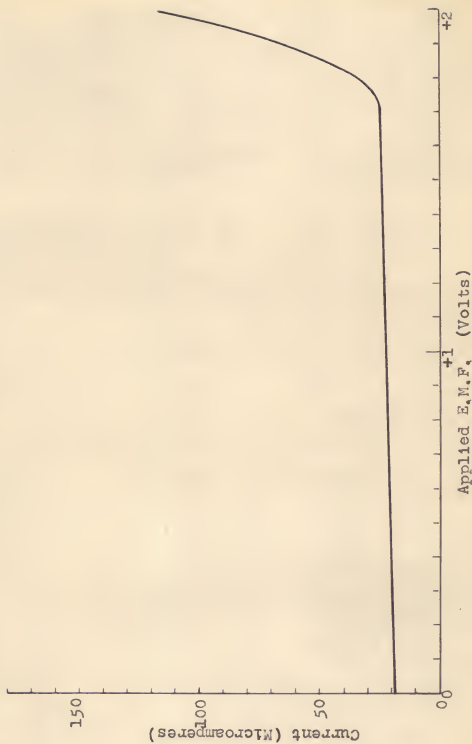


Figure 8. Polarogram of 0.1 M  $\text{KNO}_3$  in H-cell {cell (2)} after the reference cell compartment had been freed of oxygen.

When oxygen was removed, all polarographic waves were eliminated over a range of  $-2.0$  v. applied to  $+1.8$  v. applied. At  $-2$  v. the usual potassium ion discharge occurred at the dropping mercury electrode (Figure 9).

Oxygen was replaced in the solution by bubbling oxygen gas from a tank through the cell for a few minutes. When the solution was electrolyzed, a large wave occurred at about  $+0.4$  volts applied which exceeded the current limit of the recorder (Figure 10).

When the potential difference between the two waves was measured, a value of about  $0.90$  v. was found. It is interesting to note that Kolthoff<sup>5</sup> reported the half-wave potential of the cathodic oxygen wave as  $-0.05$  v. versus S.C.E. and that of the peroxide wave as  $-0.90$  v. versus S.C.E. This is a potential difference of  $0.85$  v. and is in fair agreement with the potential between the two waves on the anodic side.

Apparently the presence of oxygen in the solution which is in contact with the pool electrode is the significant factor determining the appearance or absence of these two waves. The polarographic cell is no different from any other electrolytic cell. When a negative potential is applied to the dropping mercury electrode, reduction tends to occur at this electrode, oxidation at the pool electrode. Similarly with reversed polarity, the oxidation occurs at

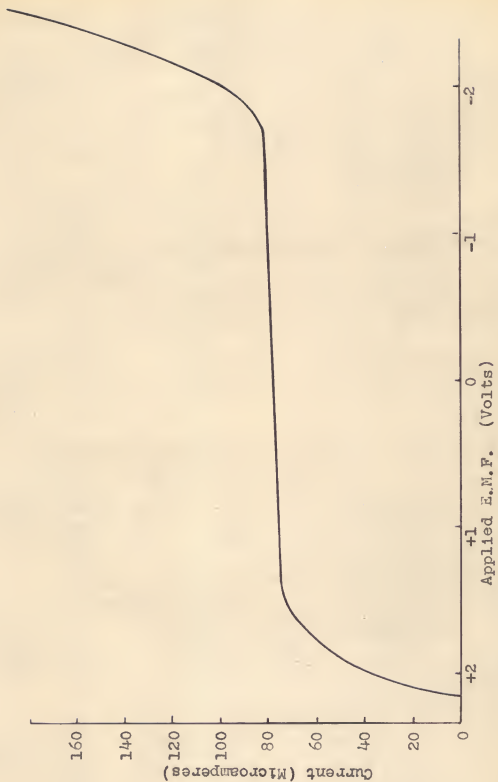


Figure 9. Polarogram of oxygen free 0.1 M KNO<sub>3</sub> in cell (3).



Figure 10. Polarograms of 0.1 M  $\text{KNO}_3$  electrolyzed in cell (2): Curve 1. Equilibrium oxygen; Curve 2. No oxygen; Curve 3. Oxygen bubbled into the solution from a cylinder of gas.

the dropping electrode and the reduction at the pool electrode. The two waves on the anodic side are, therefore, due to the reduction of oxygen taking place at the pool electrode. The oxidation, occurring to an equivalent extent, proceeding at the dropping electrode must be mercury metal to mercurous ion.

The height of the wave is proportional to the amount of current drawn and hence to the amount of material reacting at the electrodes. The oxygen waves are much larger in size when the reduction occurs at the pool electrode since the area of the electrode is much greater than the area of the mercury drop. Hence, the increased surface area allows the diffusion of more material to the electrode thereby producing a wave of much increased height.

Since fairly large amounts of oxygen are reduced, subsequent runs find significantly smaller concentrations of oxygen in the solution. Thereby, waves of lesser height are produced. The waves never disappear completely for only a fractional amount of the material present is reduced each time. Also additional oxygen is continually adsorbed by the solution from the atmosphere. Addition of more oxygen increases the heights of these waves. The current is very large when the electrolyte has been in contact with pure oxygen since the solution is then saturated (or even super-saturated) with oxygen instead of just



in equilibrium with the oxygen of the atmosphere.

The potential difference between the two waves is about the same as that found between the cathodic oxygen and peroxide waves. The agreement here is much better than might be expected when the amount of material reacting is considered.

Polarographic Studies in Some Additional Electrolytes.

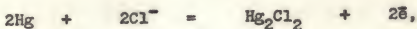
Similar waves should be found in other supporting electrolytes--in particular those that do not form insoluble or complex mercury compounds. This was found to be the case. Potassium sulphate and potassium perchlorate were found to be entirely comparable to potassium nitrate as a supporting electrolyte. The polarograms in the three solution were almost identical. The two waves were found at the same potentials and disappeared in the absence of oxygen.

When 0.1 M potassium chloride was electrolyzed in the modified H-cell {cell (3)} in the absence of oxygen, no wave was found before +1.8 v. applied. Here, too, oxygen is the important factor and the situation is analogous to that found in potassium nitrate and potassium sulphate electrolytes.

Usually, it is found that the presence of chloride gives rise to an anodic wave which is ascribed to a shift in the mercury dissolution potential because the mercury

is easier to oxidize in the presence of a substance which keeps the mercurous ion concentration low.

Any time current is drawn a reaction must occur at both electrodes. If the oxidation is



a reduction must occur at the opposite electrode. The other electrode reaction is the reduction of oxygen. If no oxygen is present than no reduction may occur and there can be no diffusion current drawn even in the presence of chloride.

In a potassium chloride electrolyte and in the presence of oxygen at a potential of about +1 volt, the surface of the mercury drop was coated with a shiny black film, the formation of the drop was distorted and the drop time varied with successive drops. The "mercury tube effect," a phenomenon noted by Bockris and Parsons<sup>2</sup>, also occurred at about this potential. These effects were not found when the solution was thoroughly scrubbed with pure nitrogen.

#### Reduction of Metallic Ions at the Pool Electrode.

Since it was possible to reduce oxygen at the mercury pool electrode, it was deemed likely that other ions also might be reduced. It was expected that the currents would be much greater when the reductions occurred at the mercury

pool than when they occurred at the dropping mercury electrode.

Experiments were run with four metallic ions in the modified H-cell {cell (3)}. These ions were cadmium II, zinc II, chromium III, and thallium I. Each of these was dissolved as the nitrate in 0.1 M potassium nitrate to produce solutions  $10^{-4}$  M in the metallic ion. Oxygen was then removed from the solutions. Waves were produced in each case exactly as anticipated. Figures 11, 12, 13 and 14 show, respectively, these waves. The voltage range covered was 0 to +2 v. applied.

The good amalgam formers, cadmium, zinc and thallium produced well defined polarographic waves when reduced at the pool electrode. A maximum, however, was found on each wave. Chromium formed a poorly defined wave, as might have been anticipated, since the electrode surface of the pool is not renewable as is the case with the D.M.E.

Table II lists the half-wave potentials of these ions in a supporting electrolyte of potassium nitrate. Table III lists the half-wave potentials of several metallic ions and oxygen when the reduction reactions occurred at the mercury pool electrode. These potentials were not accurately determined. The measurements were taken directly from graphs rather than as potentiometer readings.

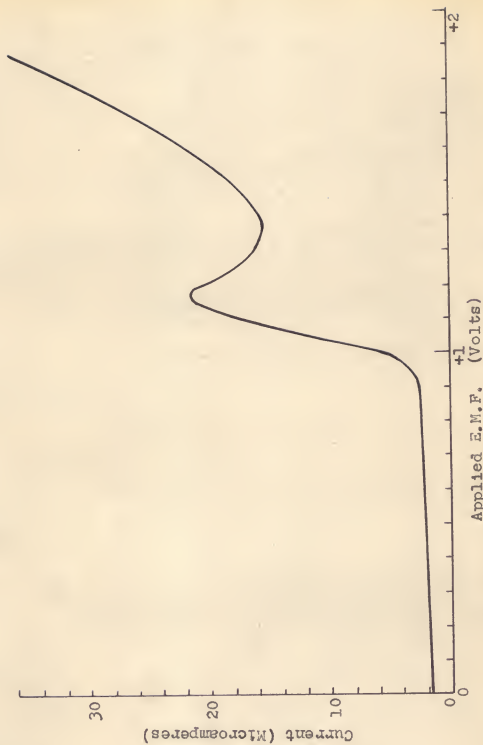


Figure 11. Polarogram of  $10^{-4}$  M  $\text{Cd}^{++}$  in 0.1 M  $\text{KNO}_3$  supporting electrolyte.

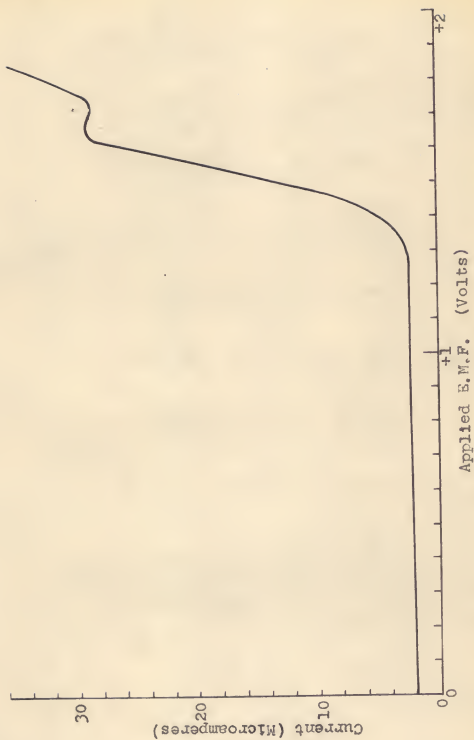


Figure 12. Polarogram of  $10^{-4}$  M  $Zn^{++}$  in 0.1 M  $KNO_3$  supporting electrolyte.

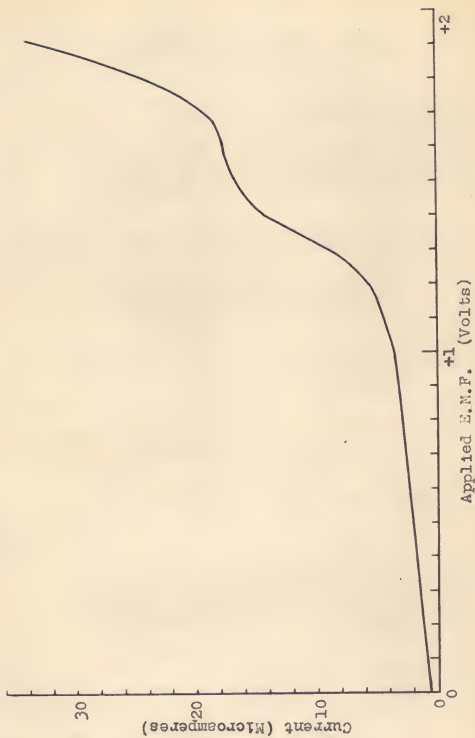


Figure 13. Polarogram of  $10^{-4}$  M  $\text{Cr}^{+++}$  in 0.1 M  $\text{KNO}_3$  supporting electrolyte.

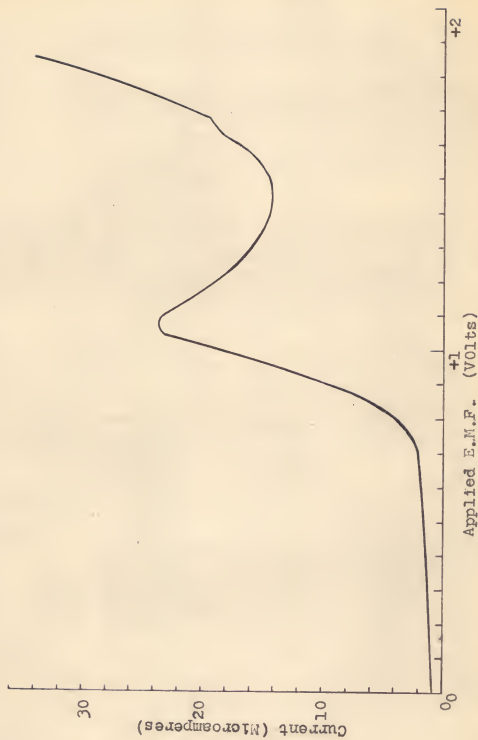


Figure 14. Polarogram of  $10^{-4}$  M  $Tl^{+}$  in 0.1 M  $KNO_3$  supporting electrolyte.

TABLE II

HALF-WAVE POTENTIALS OF SOME METALLIC IONS IN POTASSIUM  
NITRATE SUPPORTING ELECTROLYTES

Ion	Concentration of Electrolyte	Half-Wave Potential <u>vs.</u> S.C.E. <sup>7</sup>
Tl <sup>+</sup>	0.1 M	-0.46 V
Zn <sup>++</sup>	0.01 M	-0.99 V
Cd <sup>++</sup>	0.1 M	-0.58 V

TABLE III

HALF-WAVE POTENTIALS OF SOME SUBSTANCES IN 0.1 M  
POTASSIUM NITRATE WHEN THE REDUCTION OCCURRED AT THE  
POOL ELECTRODE

Ion or Substance	Concentration	Half-Wave Potential <u>Volts Applied</u>
Tl <sup>+</sup>	10 <sup>-4</sup> M	+0.96 V
Zn <sup>++</sup>	10 <sup>-4</sup> M	+1.52 V
Cd <sup>++</sup>	10 <sup>-4</sup> M	+1.04 V
O <sub>2</sub> (first wave)	Equilibrium	+0.56 V
O <sub>2</sub> (second wave)	Equilibrium	+1.46 V



It is interesting to note that the differences in potentials between the various waves as measured with the reduction occurring at the dropping mercury electrode is quite similar to the corresponding potential differences as the various species are reduced at the pool electrode. Table IV shows the potential differences between thallium, cadmium and the oxygen waves with respect to the zinc waves for both electrodes.

TABLE IV

COMPARISON OF THE POTENTIAL DIFFERENCE BETWEEN THE HALF-WAVE POTENTIAL OF ZINC ION AND THE VARIOUS REDUCIBLE SPECIES AT THE POOL ELECTRODE AND AT THE DROPPING ELECTRODE

Species Compared	Potential Difference Pool Electrode	Potential Difference D.M.E.
$\text{Cd}^{++}$	0.48 V	0.41 V
$\text{Tl}^{+}$	0.46 V	0.43 V
$\text{O}_2$	0.06 V	0.09 V
Peroxide	0.96 V	0.84 V

Effect upon Current Drawn by Variation of the Area of the Pool Electrode. Since it had been postulated that the large currents drawn upon positive polarization of the D.M.E. are due to the large area of the pool as compared to the area of the drop, variation in surface of either electrode should cause a change in the amount of current drawn during a reaction. Cell (4) (See Page 9) was

designed to change the surface area of the pool electrode. A solution,  $10^{-4}$  M in cadmium ion and 0.1 M in potassium nitrate, was divided into two aliquot portions. Each of these aliquots was deoxygenated and electrolyzed. The electrode area in the first case was  $387 \text{ mm}^2$  and in the latter  $160 \text{ mm}^2$ . These curves are shown in Figure 15. The areas, wave heights and ratios are tabulated in Table V.

TABLE V

VARIATION OF THE HEIGHT OF THE ANODIC CADMIUM WAVE  
WITH THE AREA OF THE POOL ELECTRODE

	Pool Area	Wave Height
		Sensitivity, 0.600 amp/mm
	$387 \text{ mm}^2$	27.9 mm
	$160 \text{ mm}^2$	9.1 mm
Ratios	$387/160 = 2.42$	$27.9/9.1 = 3.07$

The wave height is not directly proportional to the pool electrode area. This is not surprising since the currents drawn are large, the pool surface is not continually renewed and the measurements of area were crude. The current ratio is somewhat larger than might be anticipated from the area ratio. Since the surface area increases with the square of the diameter, this discrepancy may at least partially be accounted for by the failure to include the areas of the meniscuses in the measurements.

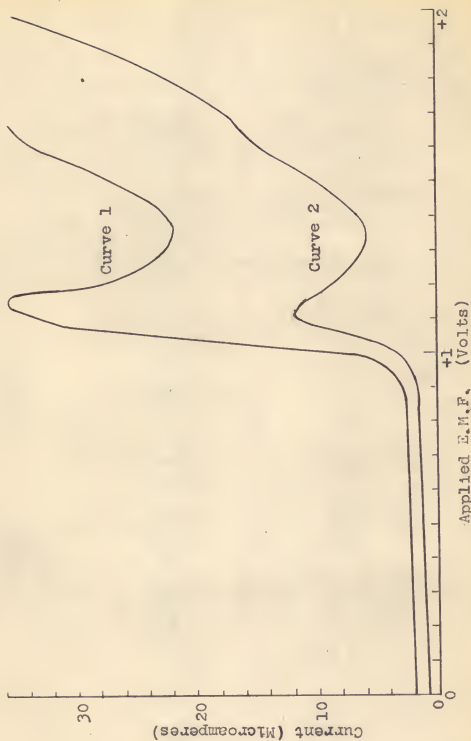


Figure 15. Polarograms of  $10^{-4}$  M  $\text{Cd}^{++}$  in 0.1 M  $\text{KNO}_3$  showing variation of current with the area of the pool electrode: Curve 1. Area of the pool is 397 mm<sup>2</sup>; Curve 2. Area of the pool is 150 mm<sup>2</sup>.

Again the relationship between electrode area and wave height was observed when  $10^{-4}$  M zinc ion in 0.1 M potassium nitrate was reduced at the pool electrode and at a different applied potential at the D.M.E. At the same sensitivity the reduction at the pool electrode drew a current of 27.0 microamperes and at the D.M.E. the current drawn was 0.90 microamperes. These waves are shown in Figure 16.

The calculation of the surface area of the pool electrode is surely crude as has been previously stated. The approximation of a value for the surface of a constantly changing drop is even more difficult. The mass of a single was known from the capillary constant determination. The surface area of the drop was approximated by assuming the drop to be a perfect sphere with a density of 13.6 g/cc. At zero potential applied the surface area of the drop was calculated to be  $3.64 \text{ mm}^2$ . The area of the pool was  $346 \text{ mm}^2$  and the ratio of the pool area to the drop area was 95. This is at least the same order of magnitude as the current ratio, 30.

The Reduction of Potassium Ion at the Pool Electrode.  
Since the oxygen, peroxide, thallium, zinc and cadmium waves had been found to occur under proper conditions at either the pool or the dropping mercury electrode, the large current drawn at about +1.9 v. applied was undoubtedly

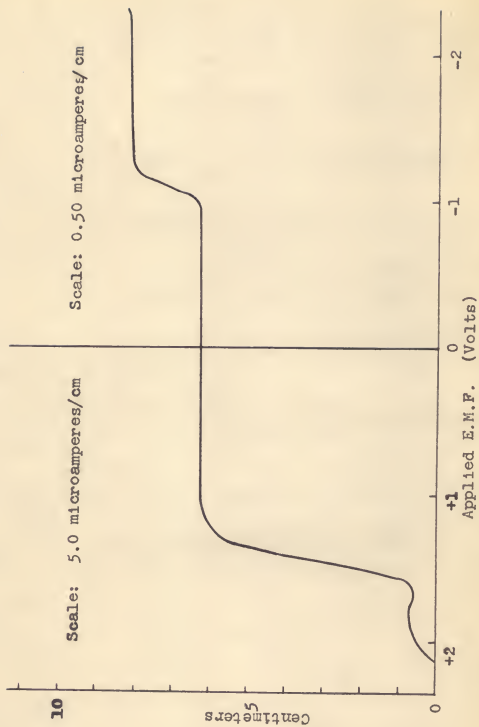


Figure 16. Polarogram of  $\text{Zn}^{++}$  in 0.1 M  $\text{KNO}_3$  supporting electrolyte showing the reduction at both the D.M.E. and the mercury pool electrode.

due to the potassium ion reduction at the pool electrode. The decomposition potential was frequently somewhat lower when the reduction occurred at the pool electrode since the amount of potassium ion reduced was quite large. It is also true, for any cathodic reduction, that the decomposition potential of the wave becomes lower with increasing concentration of the material being reduced.

At times it appeared that an inflection point existed in the wave referred to above as the reduction of potassium ion at the pool electrode. This inflection may be seen in both Figures 14 and 15. This may have been due to the presence of another ion which would also partially explain the low decomposition potential of the potassium ion. Only a very small amount of impurity need be present since the sensitivity to concentration is greater at the pool electrode than at the dropping mercury electrode.

Other than postulating an impurity in the solution, the hydronium ion is the only possible species present which is reducible near this potential. Meites<sup>8</sup> gives the half-wave potential for the hydronium ion at the D.M.E. as  $-1.58$  v. versus the S.C.E. Pure potassium nitrate (0.1 M) supporting electrolyte and the same potassium nitrate solution with small added amounts of nitric acid were electrolyzed. This caused the build up of a wave at potentials slightly less positive than the potassium ion reduction. This is illustrated by Figure 17.

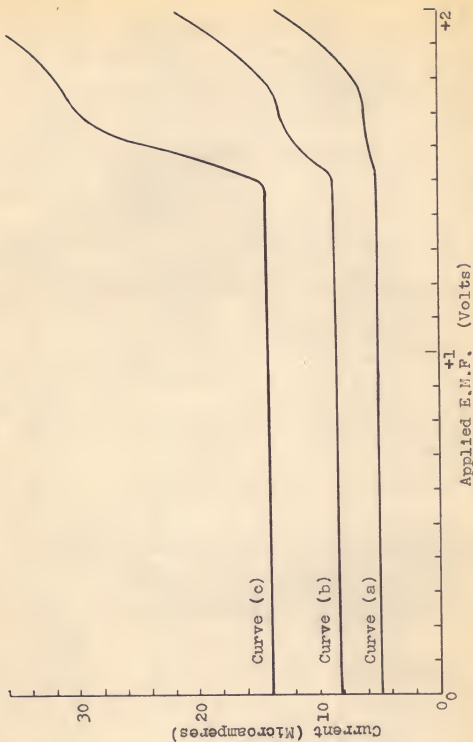


Figure 17. Polarograms of 0.1 M  $\text{KNO}_3$  with (a) no nitric acid added, (b)  $10^{-4}$  M nitric acid added and (c)  $10^{-3}$  M nitric acid added.



Addition of a Reducible Ion in the Presence of Chloride to Produce a Halide Wave. In the absence of oxygen in the electrolyte solution surrounding the pool electrode, no chloride wave was found when even 0.1 M potassium chloride was electrolyzed.

If the reason that a halide wave does not appear in the absence of oxygen is that there is no ion present to be reduced at the pool electrode, addition of a reducible ion should allow the reappearance of the halide wave. Figure 18 shows polarograms of solutions containing 0.1 M potassium nitrate,  $5 \times 10^{-4}$  M cadmium nitrate and either 0,  $2 \times 10^{-4}$  M, or  $4 \times 10^{-4}$  M potassium chloride. A small wave was found a few hundredths of a volt less positive than that of the cadmium wave which is proportional to the chloride concentration. The electrode reactions now are

(1) at the dropping mercury anode



and

(2) at the pool electrode





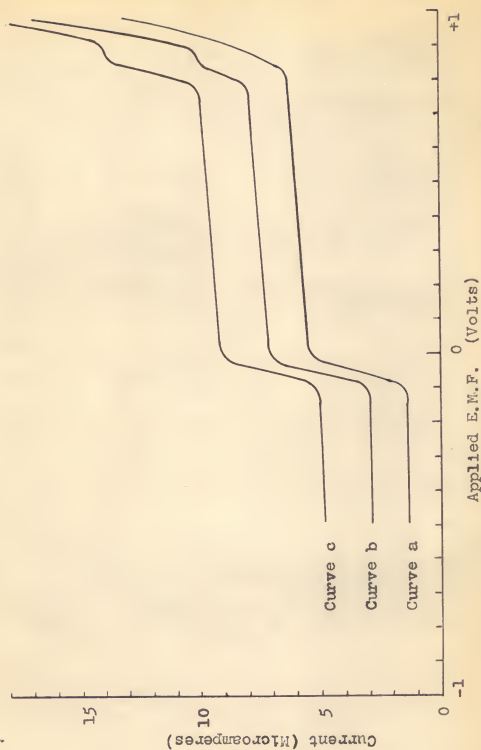


Figure 18. Polarograms of 0.1 M potassium nitrate,  $5 \times 10^{-4}$  M cadmium nitrate and (a) no KCl added, (b)  $2 \times 10^{-4}$  M KCl added and (c)  $4 \times 10^{-4}$  M KCl added.

#### IV. SUMMARY

The polarographic cell must be considered in the same manner as any conventional electrolytic cell. Upon reversal of the polarity of the electrodes the electrode processes in a Heyrovsky cell are also reversed. If a reduction was occurring at the dropping mercury electrode and an oxidation at the pool electrode, then when the polarity of the applied potential is changed the same reduction would occur now at the pool and the same oxidation at the D.M.E. However, some of the products formed at the dropping mercury electrode are carried with the falling drops into the pool and may produce inconsistent pool electrode reactions. This difficulty is avoided by separating the pool electrode and the pool of used mercury.

The large wave referred to in the polarographic literature as the mercury dissolution wave is due to the following electrode processes in a Heyrovsky cell.

At the pool cathode



and at the dropping mercury anode in an inert electrolyte



or, in an electrolyte such as potassium chloride



In the absence of oxygen or other reducible species no

reaction may take place, and no wave occurs until a potential is reached which permits reduction of the potassium ion.

The reductions occurring at the pool electrode draw much larger currents than those which occur at the mercury drop. The pool electrode has a much greater surface area than the drop thereby permitting more ions or molecules to diffuse to the pool in a given time. Variation of the area of the pool electrode causes a similar variation in the height of the polarographic waves. Since so many ions react at the pool, the concentration of the ion is significantly altered by each electrolysis cycle.

Other substances also may be reduced at the pool cathode. The following species have been found to produce waves:  $O_2$ ,  $H_2O_2$ ,  $Tl^+$ ,  $K^+$ ,  $H_3O^+$ ,  $Zn^{++}$ ,  $Cd^{++}$  and  $Cr^{+++}$ . The half-wave potentials fall in the same sequence and at practically the same potential differences from each other whether reduced at the pool or at the mercury drop.

Exhaustion of a reducible substance at the pool cathode may be responsible for many of the anomalies noted during the electrolysis of halides and related substances. It may be possible to extend greatly the usefulness of these waves by reducing the oxygen concentration to a very low level and adding some reducible metallic ion.

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## BIOGRAPHICAL NOTES

George Gilbert Long was born in Cincinnati, Ohio, on July 12, 1929. He attended Indiana University from 1947 to 1951 and received his Bachelor of Arts degree in Chemistry. He received a Master of Science degree in Agricultural and Biological Chemistry from North Carolina State College of Agriculture and Engineering in June of 1953. In September of 1953 he entered the University of Florida to continue his graduate studies in chemistry.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 26, 1957

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Dean, College of Arts and Sciences

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